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Room temperature hydrogen sensor with ultrahigh-responsive characteristics based on $Pd/SnO_2/SiO_2/Si$ heterojunctions

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ABSTRACT

A series of $Pd/SnO_2/SiO_2/Si$ heterojunction sensors were produced using magnetron sputtering method. It is found that the $Pd/SnO_2/SiO_2/Si$ heterojunction exhibits ultrahigh H_2 response of ~17363% to 1.0% H_2 at room temperature, and has fast response and recovery, excellent stability and selectivity. Therefore, this kind of heterojunction may be a promising candidate for effective H_2 detection at room temperature. The H_2 response characteristics and the optimum operating voltage of the sensors is modulated by the interface barrier potential between SnO_2 and Si, which can be understood by the interfacial energy band characteristics of the $Pd/SnO_2/SiO_2/Si$ heterojunction.

1. Introduction

Hydrogen (H_2) is colorless, odorless, explosive and extremely flammable under a concentration range of 4% – 75%. Meanwhile, H_2 as a kind of new-type and clean fuel has become one of the best choice to replace fossil energy in future. Therefore, accurate and fast detection of H_2 become especially necessary and important in industrial applications which adopted H_2 in energy production. At present, the detection of a trace of H_2 leakage has become a crucial issue for vigilant control, so the development of high-response gas sensor for low H_2 concentration has aroused much concern. SnO_2 is an *n*-type semiconducting metal oxide and has been widely used for gas-sensing applications by measuring the change of the resistance upon exposure to reducing gases (H_2, CO, SO_2, NH_3, CH_4, H_2S, etc.). Moreover, it is very attractive because of their distinct advantages such as low operating temperature, limit of detection, high sensitivity, fast response and recovery, high selectivity, high reproducibility and compatibility with micro-fabrication processes, etc. [1–7]. In addition, its gas sensing performances can be further catalytically enhanced by doping noble metals such as Pd [8–13], Au [2], Ru [14] and Pt [15–17]. In particular, Pd [18–20] is one of the most versatile and most widely applied catalytic metals for enhancing the response of gas sensors toward H_2 and decreasing the sensor's optimal operating temperature.

A summary of gas sensing properties of Pd-doped SnO_2 prepared by several synthetic methods is shown in Table 1. Firstly, it is demonstrated that the mesoporous SnO_2 sensor loaded with 0.2 wt% Pd prepared by nanocasting method exhibits a H_2 response of 1250% to the 1000 ppm H_2 at 150 °C and short response/recovery times of 1 s/10 s [8]. It was also reported that the H_2 response and optimum operating temperature of the mesoporous SnO_2 sensors are significantly improved with Pd incorporation. Wen group developed H_2 sensor based on $Au/Pd/SnO_2$ by electroless deposition [10]. It is found that the SnO_2–Pd–Au nanocomposite film sensor has a response of 1.1% toward 134–1469 ppm H_2 at room temperature (RT), and has good stability and repeatability. Zhang et al. fabricated the Pd/SnO_2 nanofibers H_2 sensors by electrospinning and calcination techniques [12]. It is demonstrated that the sensors show excellent H_2 sensing properties including high sensor response (9000% at 10000 ppm) and extremely fast response/recovery time (~9 s) at high operating temperature (280 °C). Lee et al. prepared SnO_2 nanorod thin film by PECVD, which surface was modified with Pd nanoparticles [21]. It is found that the Pd/SnO_2 nanorod thin film sensor exhibits a response of 1000% to 1000 ppm H_2 at 150 °C and high selectivity against CO, H_2, NH_3 and ethanol in dry air at 300 °C.

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Table 1
Summary of sensing performances of Pd-doped SnO_2 H_2sensors.

Nanomaterials	Method/structure	Concentration (ppm)	Operating temp. (°C)	Sensing performances	
				Response	Tres/Trec (s/s)
Pd/SnO_2	Nanocasting/ mesoporous	1000	150	1250%	1/10
SnO_2–Pd–Au	Hydrothermal electroless deposition/mixed film	134–1469	RT	1.1%	<60/60~120
Pd–SnO_2	Electrospinning/ composites nanofibers	10,000	280	9000%	9/9
Pd/SnO_2(on SiO_2/Si substrate)	PECVD/nanorod films	1000	150	1000%	<120/<900
Pd–SnO_2 (on SiO_2 substrate)	RF magnetron sputtering/thin film	10000	400	500%	–
Pd–ITO	R.F magnetron sputtering/nano-grained thin film	1000	300	0.8%	<5/–
Pd/SnO_2(on SiO_2/Si substrate)	R.F magnetron sputtering/thin film	10000	RT	17363%	37/24(This work)

RF-magnetron sputtering method is a popular and simple method to prepare kinds of oxide films. For example, Choi et al. investigated the H_2 sensing properties of highly oriented polycrystalline 0.5 wt% Pd/SnO_2 on SiO_2 substrate, which was prepared using RF-magnetron sputtered method at a range of operating temperature from 400 °C to 550 °C [22]. The film shows a fairly high H_2 response at 400 °C (500% at 10,000 ppm H_2) and the sensor response decreases with increasing sensing temperature. Yoo et al. deposited nano-grained indium tin oxide (ITO) thin films catalyzed by Pd on the alumina substrate at ambient temperature or 300 °C using an RF-magnetron sputtering system and then annealed at 650 °C for 1 or 4 h in air [23]. The ITO (In_2O_3:SnO_2 = 20:80) sensors showed a H_2 response of 0.8% to 1000 ppm H_2. On the whole, most of SnO_2 sensors show the optimum sensing properties at high temperature. Moreover, the comparison of H_2 gas response between undoped and Pd-doped SnO_2 films revealed that the Pd-doping shifted the optimum sensing temperature to a lower value.

In addition to the above type resistance sensor, it is well known that oxides based gas sensor in the forms of Schottky diodes [24–26], and *p*-*n* or *n*-*n* diodes [27–30] have widely used. Yu fabricated a Pt/ZnO/SiC nanostructured Schottky diode. It is shown that the Pt/nanorod ZnO/SiC based Schottky diode is a highly sensitive gas sensor when utilized in the reverse bias condition [24]. Quang et al. fabricated monolayer graphene (GP)/SnO_2 nanowire (NW) Schottky junctions devices, which showed an outstanding NO_2 gas sensing properties [25]. Hyodo found that Au/Pt/TiO_2 sensor showed the largest H_2 response (~1000% at 1% H_2) among all the Au/M/TiO_2 sensors annealed at 600 °C [26].

In addition, gas sensors of oxide based *p*-*n* or *n*-*n* diodes are also investigated widely. Lee et al. prepared a series of SnO_2 based *p*-*n* or *n*-*n* junctions such as *p*-Cr_2O_3/*n*-SnO_2 [27], *p*-GO/*n*-SnO_2 [28] and *n*-SnO_2/*n*-ZnO [29] junctions. It was demonstrated that functionalization with *p*-Cr_2O_3 nanoparticles greatly improved the reducing gas-sensing properties of *n*-SnO_2 nanowires [27]. It is also found that *n*-SnO_2 nanofibers can greatly improved gas-sensing performances when loaded with an optimized amount of *p*-reduced graphene oxide nanosheets, which can result in a 20-fold higher sensor response than that of pristine SnO_2 nanofibers [28]. In addition, SnO_2-ZnO composite nanofibers were fabricated using an electrospinning technique. The composite nanofiber sensor showed better sensing selectivity to H_2 gas than did their pure components [29]. Moreover, it is reported that Au–SnO_2/ZnO nanorods gas sensor shows fast response to triethylamine at near room temperature [30].

At present, our groups investigated a series of C/Si heterojunctions (*p*-*n* or *n*-*n* diodes) which show much better gas response than that of carbon film, due to an excellent "interfacial amplification effect" of C/Si heterojunction [31–36]. Based on the above discussion, we put forward an idea to improve the H_2 gas response of oxide films. It has been demonstrated that the TiO_2 films/SiO_2/Si heterojunctions showed excellent H_2 sensing properties, due to the interfacial amplification effect [37]. Herein, we fabricated a series of $Pd/SnO_2/SiO_2$/Si heterojunctions using magnetron sputtering methods. It is found that the $Pd/SnO_2/SiO_2$/*p*-Si heterojunction can show an ultrahigh response (~17363%) to 1% H_2 with appreciable short response time of 37 s and recovery time of 24 s at RT. The heterojunction shows excellent selectivity to N_2, NO_2, O_2, CH_4, CO_2, NH_3 and H_2 and stability. Therefore, the $Pd/SnO_2/SiO_2$/Si heterojunction sensor is one of the most promising candidates for highly sensitive, good selective detection of H_2 at RT.

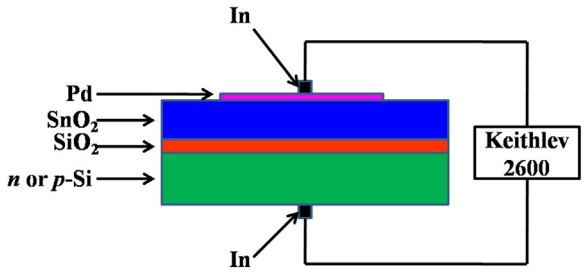

Fig. 1. The schematic illustrations of the *I*–*V* measurement of $Pd/SnO_2/SiO_2$/Si heterojunctions.

2. Materials and experiments

2.1. Synthesis and characterization of $Pd/SnO_2/SiO_2$/Si heterojunctions

The fabrication of $Pd/SnO_2/SiO_2$/Si heterojunction sensors can be briefly described as follows: firstly, a SnO_2 film was grown on Si <100> substrate (10 mm × 10 mm) with native oxide layer (1.2 nm) [38] using magnetron sputtering method. The resistivities of *p*-Si or *n*-Si substrates (the forty-sixth institute of Ministry of Electronics Industry, Tianjin, China) are 0.1–1 Ω cm or 0.01–0.02, 0.1–1, 1–3 Ω cm, respectively. The Si substrates were successively cleaned in ethanol and acetone solution using ultrasonic (Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China) for 5 min, in the cleaning process no etching solution was used. Sn target is purchased at Beijing Jinyan Zhong new material Co., Ltd., Beijing, China. Before depositing SnO_2 film, the sputtering chamber was pumped below 2×10^{-4} Pa and Si substrate was kept at RT. The working gas during deposition was mixed gas of argon and oxygen, two kinds of gas proportion is 1:1. The total gas pressure is 5 Pa, both oxygen and argon partial pressures are 2.5 Pa. In the deposition process, gas pressure, deposition power and time were 5 Pa, 40 W and 10 min, respectively.

Secondly, the Pd film was deposited on the surface of SnO_2/SiO_2/Si utilizing a metal mask from a Pd target (Beijing Mountain Technical Development Center, Beijing, China) using DC magnetron sputtering. In the deposition process, argon gas pressure, deposition power and time were 3 Pa, 40 W and 2 min, respectively. The substrate was still kept at RT. Thus the $Pd/SnO_2/SiO_2$/Si heterojunction was prepared and its structure is illustrated in Fig. 1. The size of Pd film is 5.0 mm × 5.0 mm. The Pd film was used as sensitive layer and it has been characterized that